

METHOD OF FABRICATING A COMPOSITE ORGANIC MEMBRANOUS SUBSTANCE

FIELD OF THE INVENTION

The present invention relates to a method of fabricating
5 a composite organic membranous substance which comprises
spray-coating a reticulate or bar-like material with a
solvent-free two-component type curable resin, a composite
organic membranous substance comprising a membranous organic
resin and a reticulate or bar-like material, and a method of
10 corrosion-proofing a concrete substrate which comprises using
said composite organic membranous substance.

PRIOR ART

The composite organic membranous substance is made up of
15 not less than two component materials, namely a resin and other
auxiliary materials as a reinforcement, etc. The composite
organic membranous substance has heretofore been in use broadly
as a reinforced resin membrane. For example, a glass
fiber-reinforced organic membrane and an organic membrane
20 carrying a reinforcing lining are so far available.

The known production technology for a glass fiber-
reinforced organic membrane includes a reactive injection
molding method in which a reactive resin composition containing
glass filaments compounded therein in advance is cast in a mold
25 (R-RIM process) and a reactive injection molding method in which
a glass cloth or mat is set in a mold in advance and a reactive
resin composition is then poured into the mold (S-RIM process).

In the R-RIM process, glass filaments are oriented in the
direction of flow of the resin being injection-molded so that
30 a sufficient strength can be obtained in the direction of
orientation of glass filaments but virtually no reinforcing
effect can be expected in the direction perpendicular to the
direction of orientation of glass filaments. In the S-RIM
process, there occurs no local variation in the distribution
35 of strength owing to orientation of the reinforcement so that

a uniform distribution of strength can be attained but this process requires a large-sized injection molding machine/metal mold.

Both of these processes are intended for mass production
5 of the same item using a more or less large equipment/metal mold and are quite unsuited for multiple-item, small-lot production. Moreover, there is a limit to the size of product that can be produced so that large-scale products cannot be fabricated.

For the fabrication of an organic membrane lined with a
10 reinforcement for the water-proofing, corrosion-proofing, reinforcing, and/or prevention of slide-down of concrete structures or the like, the FRP lining technology is known which utilizes a matrix resin such as vinyl ester resin, polyester resin, epoxy resin or the like and a reinforcement such as glass
15 cloth/mat, carbon filament cloth/mat, aramid filament cloth/mat or the like. These methods invariably use a cloth or mat as a lining material.

The conventional lining method comprises impregnating a reinforcing liner material with a resin capable of forming a
20 resin membrane lined with the reinforcement. In this method, the resin for use must be of low viscosity for efficient impregnation. However, low-viscosity resins naturally have the drawback of poor film-forming properties. Therefore, there has been the technical problem to be solved for
25 reconciling the conflicting requirements, namely low viscosity and good film-forming properties. The general approach toward solving the above problem has been to adjust the resin viscosity by formulating a low molecular weight monomer in the resin composition or adding an organic solvent and carry out a series
30 of four steps, namely i) application of a resin composition, ii) superimposition of a reinforcing liner on the resin, iii) impregnation of the liner with the resin composition and iv) final coating with the resin composition. In this process, the use of volatile components and an organic solvent is
35 indispensable but these substances are hazardous to health and

environment. As an additional disadvantage, this process involves a large number of steps as mentioned above. Moreover, the conventional lining technology can hardly be applied to a high-viscosity resin composition.

5 The problem with the prior art, which is encountered in its application to concrete structures, for instance, is the fact that such a liner-reinforced resin membrane suffers a marked loss of adhesion to concrete in the presence of moisture. Therefore, in the covering of a concrete surface for corrosion
10 inhibition with an organic material, it is common practice to control the water content of concrete to about 8% or less and, in addition, interpose a primer (undercoat) layer between the concrete surface and the organic coating. However, it is not
15 easy to control the water content of concrete to about 8% or less in the field where various restrictions are imposed. Moreover, when a concrete structure is rich in water or under the condition of dew condensation, a primer, if ever applied, does not insure a sufficient adhesion between the concrete and the resin coating.

20 Of course, the above problems arise not only in applying the conventional lining technology but also in using a corrosion protection system in which a polyurea resin is directly sprayed against the concrete surface.

 The foregoing is a serious drawback in the surface
25 treatment of concrete in the field. For example, it is quite time-consuming and costly to dry the concrete surface well by means of a heater having a blower means, apply an undercoat, and carry out the above-mentioned four steps. Therefore, this method cannot be selected for repair projects with
30 comparatively short contact terms, for example in the repair work on a sewage system for which the flow of water may be arrested only for a few hours a day. Moreover, it is not rare that insufficient drying results in the blistering, swelling or exfoliation of the applied membranous substance.

SUMMARY OF THE INVENTION

Accomplished to overcome the above problems, the present invention has for its object to provide a novel method of fabricating a composite organic membranous substance using a reticulate or bar-like material and a solvent-free two-component type curable resin and a method of preventing corrosion of concrete substrates without causing defects such as blistering, swelling and exfoliation even when the concrete surface is moist and can be carried through in a short period of time.

A first aspect of the present invention relates to a method of fabricating a composite organic membranous substance comprising a membranous organic resin and a reticulate or bar-like material

which comprises coating a solvent-free two-component curable resin on a reticulate or bar-like material in a sheet form by two-component collision-mixing spray coating, and allowing the resin to cure and to thereby form a membranous organic resin integral with said reticulate or bar-like material.

A second aspect of the present invention relates to a composite organic membranous substance obtained by said method.

In accordance with one embodiment, by fixing a reticulate or bar-like material on a substrate surface in advance, a composite organic membranous substance can then be formed on said surface.

A third aspect of the present invention further relates to a method for corrosion-inhibition of concrete.

which comprises fixing a reticulate or bar-like material in position on a concrete surface and coating a solvent-free two-component curable resin over said reticulate or bar-like material by two-component collision-mixing spray coating, and allowing the resin to cure and to thereby form, over said concrete surface, a composite thick membranous organic resin comprising at least part of said material.

The inventors of the present invention found that when a fast-curing solvent-free two-component curable resin is directly sprayed against a reticulate material or a bar-like material disposed on a plane, the interstitial spaces of the material are completely filled up with said resin and, in addition, not only the coated side of the reticulate or bar-like material but also the reverse side thereof is simultaneously covered. The present invention has been developed on the basis of the above finding.

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BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 shows schematic sectional elevations of the composite organic membranous substances according to the invention.

15 The present invention is now described in detail.

DETAILED DESCRIPTION OF THE INVENTION

In the method of fabricating a composite organic membranous substance according to the present invention, a solvent-free two-component curable resin is applied in a sheet form to a reticulate or linear material by two-component collision-mixing spray coating and allowed to cure and to thereby give a membranous substance as one.

20 The reticulate material mentioned above is not particularly restricted in raw material, shape or construction but can be suitably selected according to the intended application. Regarding the raw material, for instance, it may be selected from among mesh screens of iron, aluminum, stainless steel and other metals; reticulate materials of inorganic fibers such as glass fiber, carbon fiber, etc.; reticulate materials of organic fibers such as aramid fiber; reticulate materials of various other synthetic resins such as polyvinyl chloride, polyethylene, polyester, etc.; and reticulate materials of various natural materials such as plant fibers, etc. The shape may be any arbitrary planar one or any arbitrary

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curved one. With regard to construction, a construction such that a fiber or a wire is used to weave a reticulate pattern, a construction such that a plurality of wires or bars are arranged in a grid form and bonded at points of intersection where necessary, a construction such that a sheet material is made notched in multiple positions in parallel and stretched into a grid form, a construction such that a synthetic resin or the like is molded in a grid form, and a construction such that a sheet material is punched in a grid form may be mentioned as examples.

The plurality of the bar-like material as mentioned above may be used by arranging on a plane. The bar material is not particularly restricted but can be judiciously selected according to the intended application. For example, it may be a bar-like material comprising any of the materials mentioned above.

In the present invention, the mode of integrating the resin with the reticulate or bar-like material is not particularly restricted but includes various modes. For example, there is the mode illustrated in Fig. 1(a) wherein the resin to be applied penetrates through the meshes or interstitial spaces of the reticulate material and protrudes some distance on the reverse side of the coated reticulate material so that the material is embedded either partially or completely in the resin and, thus, reticulate or bar-like material is served as a core, the modes shown in Fig. 1(b) and (c) wherein the resin to be applied penetrates through the meshes or interstitial spaces of the material and protrudes locally on the reverse side of the material so that the material is partially surrounded and embedded by the resin, and the mode illustrated in Fig. 1(d) wherein the resin is applied from both sides of the reticulate or bar-like material to thereby embed a part of or all of the material so that the material is served as a core.

The mesh size of said reticulate material and the

interstitial spaces of said bar-like material are not particularly restricted if only they are suited for the object of the invention. Generally, however, it is good practice to pay attention to spray coating conditions and characteristics of the resin, for example the application viscosity of resin, and select the mesh size or spaces so that, when the resin is spray-coated on the reticulate or bar-like material taken the form of a sheet form and, at the same time, is integrated with the reticulate or bar-like material. In the case of a reticulate material, for instance, the mesh size is preferably not greater than 10 mm, for it will then be generally easy to form an uninterrupted continuous membrane. There is no particular lower limit to the mesh-size of said reticulate material or the interstitial spaces of the bar-like material. However, because of the need for integration with the membranous organic resin, said meshes or spaces are preferably of a size such that at least part of the resin may protrude into the meshes or interstitial spaces. The more preferred mesh size of reticulate material or interstitial spaces of the bar-like material are 1 to 5 mm and the still more preferred range is 3 to 5 mm.

Preferably, said reticulate or bar-like material is capable of maintaining its structure and arrangement so that the resin can be applied in a sheet form. Therefore, where necessary, the material may be attached to a support or provided with such a support for maintaining its structure or arrangement.

The solvent-free two-component curable resin mentioned above is not particularly restricted if only it may form a membranous organic resin on spray-coating. Generally, such a composition may comprise a main component and a curing agent component which are to be admixed in spray coating to initiate a curing reaction, and a preferred composition comprises an isocyanate component (A) and a polyamine and/or polyol component (B). The membranous organic resin which can be

obtained by using a polyamine as said component (B) comprises a polyurea resin. The membranous organic resin which can be obtained by using a polyol as said component (B) comprises a polyurethane resin. On the other hand, when the component (B) is a mixture of a polyamine and a polyol, the resulting membranous organic resin comprises a polyurethane/polyurea resin membrane.

The isocyanate component (A) as mentioned above includes organic polyisocyanates, isocyanate prepolymers, and mixtures thereof.

The organic polyisocyanates as mentioned above are not particularly restricted but may be known polyisocyanates, such as aromatic polyisocyanates, aliphatic polyisocyanates and so on.

The aromatic polyisocyanates as mentioned above are not particularly restricted but include carbodiimide-modified liquid diphenylmethane diisocyanate or its partial prepolymer; 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, and a mixture thereof (hereinafter collectively referred to as TDI); diphenylmethane-4,4'-diisocyanate (hereinafter collectively referred to as MDI), polymethylene-polyphenyl polyisocyanate; and their carbodiimide- or buret-modification products.

The aliphatic polyisocyanates as mentioned above are not particularly restricted but include dicyclohexylmethane-4,4'-diisocyanate, isophorone diisocyanate, hexamethylene diisocyanate, hydrogenated xylylene diisocyanate, isocyanurated-modification products or carbodiimide-modification products of said diisocyanates, among others.

The isocyanate prepolymers as mentioned above include partial prepolymers obtainable by reacting some of the isocyanate groups in an organic polyisocyanate, such as these mentioned above, with a polyol having a number average molecular weight of 200 to 8000.

The isocyanate prepolymer as mentioned above can be obtained by heating any of said organic polyisocyanates in the

presence of a polyol under nitrogen gas at 70 to 80 °C for several hours to cause at least some of the isocyanate groups to react with the polyol. The polyol as mentioned above is not particularly restricted but includes such polyols as ethylene glycol, propylene glycol, diethylene glycol, triethylene glycol, dipropylene glycol, trimethylene glycol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 1,2-hexyl glycol, 1,10-decanediol, 1,2-cyclohexanediol, glycerol, 1,2,6-hexanetriol, 1,1,1-trimethylolpropane, 1,1,1-trimethylolpropane, etc.; and polyether-polyols available upon addition polymerization of a polyhydric alcohol, e.g. pentaerythritol, with one or more epoxides, e.g. ethylene oxide, propylene oxide, butylene oxide, tetrahydrofuran and/or the like. In the present invention, said polyol has a molecular weight of, preferably, 200 to 8000 and, more preferably, 500 to 5000. These polyols can be used each alone or as a suitable mixture.

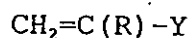
The polyamine which can be used as said component (B) is not particularly restricted but, in the practice of the present invention, it is preferable to use a mixture of a polyoxyalkylene-polyamine (a) and an active aromatic diamine (b) having no electron-withdrawing group on the aromatic nucleus and having an alkyl substituent group of not more than 5 carbon atoms in the position adjacent to the amino groups, exclusive of toluenediamine, for instance.

The polyoxyalkylene-polyamine (a) may for example be a compound having a number average molecular weight of 200 to 10000 and containing at least two aliphatically bound amino groups per molecule. Such a compound can be obtained, for example by reacting the terminal hydroxyl groups of a polyoxyalkylene polyol having at least two hydroxyl groups with ammonia in the presence of a hydrogenation-dehydrogenation catalyst at high temperature and high pressure.

The polyoxyalkylene-polyamine (a) as mentioned above includes polyoxypropylenediamines such as Jeffamine D-2000

(Huntsman Speciality Chemicals; amine equivalent ca 1000); polyoxypropylenetriamines such as Tecslim TR-5050 (Huntsman Speciality Chemicals; amine equivalent ca 1930), Jeffamine T-403 (Huntsman Speciality Chemicals; amine equivalent ca 160) and so on.

Modified polyoxyalkylene polyamines such that at least some of the primary amino groups in any of said polyoxyalkylene polyamines (a) have been converted to secondary amino groups by Michael addition reaction with an unsaturated hydrocarbon compound of the general formula:



(wherein R represents hydrogen or methyl; Y represents an electron-withdrawing group) can also be used with advantage.

The electron-withdrawing group Y is not particularly restricted but includes an ester residue, a ketone residue, a cyano residue, a substituted or unsubstituted amide residue, a sulfonic acid residue and a sulfonic ester residue, among others.

The unsaturated hydrocarbon group as mentioned above is not particularly restricted but includes esters of acrylic acid, such as n-butyl acrylate, isobutyl acrylate, t-butyl acrylate, 2-ethylhexyl acrylate, methyl acrylate, lauryl acrylate, stearyl acrylate, propyl acrylate, etc.; esters of methacrylic acid, such as n-butyl methacrylate, isobutyl methacrylate, t-butyl methacrylate, 2-ethylhexyl methacrylate, methyl methacrylate, lauryl methacrylate, stearyl methacrylate, propyl methacrylate, etc.; acrylonitrile; acrylamide; N,N'-dimethylacrylamide; ethyl vinyl sulfone; methyl vinylsulfonate, ethyl vinylsulfonate, and so on.

The above-mentioned active aromatic diamine (b) having no electron-withdrawing group on the aromatic nucleus and having an alkyl substituent group of not more than 5 carbon atoms in the position adjacent to the amino group, exclusive of toluenediamine, includes such specific compounds as 1,3-dimethyl-2,4-diaminobenzene, 1,3-diethyl-2,4-diaminobenzene,

1,3-dimethyl-2,6-diaminobenzene, 1,4-diethyl-2,5-diaminobenzene, 1,4-diisopropyl-2,5-diaminobenzene, 1,4-dibutyl-2,5-diaminobenzene, 1,3,5-triethyl-2,4-diaminobenzene, 1,3,5-triethyl-2,6-diaminobenzene, 1,3,5-tripropyl-2,6-diaminobenzene, 1-methyl-3,5-diethyl-2,4-diaminobenzene, 1-methyl-3,5-diethyl-2,6-diaminobenzene, among others. These compounds can be used each alone or in a suitable combination.

It is also possible to use modified polyamines such that at least some of the primary amino groups in said active aromatic diamines (b) having no electron-withdrawing group on the aromatic nucleus and having an alkyl substituent group of not more than 5 carbon atoms in the position adjacent to the amino group, exclusive of toluenediamine, have been converted to secondary amino groups by Michael addition reaction with said unsaturated hydrocarbon compound.

Referring to the polyamine for said component (B), the blending ratio of the polyoxyalkylene polyamine (a) to the active aromatic diamine (b) having no electron-withdrawing group on the aromatic nucleus and having an alkyl substituent group of not more than 5 carbon atoms in the position adjacent to the amino group, exclusive of toluenediamine, is 15 to 100 weight parts of (b) relative to 100 weight parts of (a). If the formulating amount of (b) is less than 15 weight parts, the membranous organic resin will be very soft and semi-adhesive so that the performance quality of the product membranous substance will be poor depending on uses. On the other hand, if the upper limit of 100 weight parts is exceeded, the membranous organic resin will be very hard and brittle so that the product membranous substance may not be useful depending on uses. The more preferred range is 20 to 40 weight parts.

On the other hand, the polyol for said component (B) is not particularly restricted. For the purpose of controlling the physical properties of the membranous organic resin, a low-molecular-weight polyol (a number average molecular

weight: 62 to 1000) and, for the main component of the organic resin layer, a high-molecular-weight polyol (a number average molecular weight: 1000 to about 10000) can be used.

The low-molecular-weight polyol mentioned above may be those polyols, among the polyols mentioned above for the production of isocyanate prepolymers, which have molecular weights within the above-mentioned range. On the other hand, the high-molecular-weight polyol is preferably a polyether polyol or a polyester polyol. The polyether polyol includes the compounds mentioned above as examples. The polyester polyol as mentioned above includes various polyester polyols which can be produced by the reaction between an aliphatic dibasic acid and an aliphatic glycol as well as polycaprolactone polyols. Such polyester polyols include those obtainable by reacting a polyhydric alcohol such as ethylene glycol, propylene glycol, diethylene glycol, 1,4-butanediol, a polyether polyol, bis(hydroxyethyl) terephthalate, glycerol, trimethylolpropane, pentaerythritol, and a mixture thereof, with a polycarboxylic acid, particularly a dicarboxylic acid or an ester derivative thereof, such as succinic acid, glutaric acid, adipic acid, dimethyl esters of the acids mentioned just above, sebacic acid, phthalic anhydride, tetrachlorophthalic anhydride, dimethyl terephthalate and the like. It is also possible to use polyesters which can be obtained by polymerizing cyclic ester lactones, such as caprolactone, in the presence of a polyol.

The solvent-free two-component curable resin comprising said isocyanate component (A) and said polyamine and/or polyol component (B) according to the present invention may further contain a third component. For example, where necessary, the conventional plasticizer, flame retardant, filler, stabilizer, coloring agent and other auxiliary agents can be employed. This third component can be directly added to said component (A) or component (B).

In the practice of the present invention, said

solvent-free two-component curable resin is spray-coated on said reticulate or bar-like material by the two-component collision-mixing spray coating technique. This spray coating may be applied to one side or both sides of the reticulate material and the bar-like material taken the form of a sheet. The membranous organic resin mentioned above is constructed by the following method; ejecting the two components of said two-component curable resin, for example said isocyanate component (A) and said polyamine and/or polyol component (B), by collision-mixing spray coating technique in such a manner that only after the curing reaction has progressed to some extent while the particles are still in suspension, applying said components to said reticulate or bar-like material in a sheet form and allowing to cure them. The isocyanate component (A) and said polyamine and/or polyol component (B) must be retained in liquid form at the application temperature. The two-component collision-mixing spray coating is preferably carried out using a high-pressure two-component collision-mixing spray system.

The high-pressure two-component collision-mixing sprayer mentioned above is not particularly restricted but includes, among others, such proportional-delivery devices as Gusmer (U.S.) H-2000, Gusmer (U.S.) H-3500, Gusmer (U.S.) FF-1600, and Toho Machinery Industry's 2-component high-pressure delivery mixing machine Model HF-100. Furthermore, as the high-pressure two-component mixing spray gun having a mechanical self-cleaning function, Gusmer (U.S.) "GX-7 gun", Gusmer (U.S.) "GX-7-400 gun", etc. can be mentioned. Furthermore, as the spray gun equipped with an air cleaning mechanism, Glass-Craft (U.S.) "Propeller Gun" can be mentioned.

Regarding the mixing ratio of said isocyanate component (A) and said polyamine and/or polyol component (B), the equivalent ratio of the amino and hydroxyl groups in said component (B) to the isocyanate group in said component (A) is preferably 1/0.7 to 1/1.5, preferred is 1/0.9 to 1/1. Outside

this range, the curing reaction does not proceed to a sufficient extent and, because of this and other reasons, the physical properties of the membranous organic resin tend to be adversely affected.

5 In the present invention, the solvent-free two-component curable resin is preferably such that when applied by said two-component collision-mixing spray coating technique, it give a tack-free time, i.e. time to drying to the extent not
10 leaving a fingerprint, of not more than 3 minutes. If this tack-free time is longer than 3 minutes, it may become difficult to apply the reticulate or bar-like material in a sheet form. There are cases, depending on the end-use of the membranous substance, in which the tack-free time is preferably still more shorter. For example, when a reticulate or bar-like material
15 is fixed in position to cover the surface of at least one kind of substrate selected from among concrete, mortar and rock, for instance and, then, the curable resin is applied over the material to fabricate said thick composite organic membranous substance, the tack-free time is preferably not more than 20
20 seconds, more preferably not more than 10 seconds, from engineering points of view. This tack-free time can be controlled by adjusting the species and amount of the compound for said component (B) and the amount of said third component such as the plasticizer. For example, the tack-free time can
25 be reduced by selecting a polyamine for said component (B).

 In the present invention, the resin mixed in the mixing spray gun is ejected at an angle of 45° to 90° against the surface of said reticulate or bar-like material. If the resin collides with the material at an angle of less than 45° , the resulting
30 membranous substance may not be homogeneous. The more preferred angle of collision is 75° to 90° .

 In the present invention, in using said high-pressure two-component collision-mixing spray system, the collision-mixing pressure is preferably set at 6 to 15 MPa.

35 Furthermore, the distance between the bar-like or

reticulate material and the mixing spray gun is preferably set at about several 10 cm to 1 m.

In the present invention, the thickness of the composite organic membranous substance is not particularly restricted but
5 can be judiciously selected according to the intended application thereof or the kind of reticulate or bar-like material used. As far as the curable resin can be applied in a sheet form, said resin may be applied in any desired thickness between 0.5 mm and 10 mm or even more, for instance, on the
10 reticulate or bar-like material. As the reticulate or wire-like material and the resin are integrated as above, the thickness of the resulting composite organic membranous substance may generally be greater than the thickness of the resin membrane formed over the reticulate or wire-like
15 material. If the thickness of the resin membrane is smaller than 0.5 mm, the durability of the membranous substance may not be sufficient. If it exceeds 10 mm, the resin consumption will be too great to be costwise acceptable. Therefore, the thickness of the resin membrane is preferably controlled within
20 the above range.

In the practice of the present invention, said reticulate or bar-like material may be preformed to the objective shape of the membranous substance, for example a flat sheet form, a curved sheet form or a three-dimensional form, and the curable
25 resin may be then directly spray-coated on such formed material to give a composite organic membranous substance having the desired shape. Uses for the membranous substance are not particularly restricted but the machine cover and duct can be mentioned as typical examples. Thus, large-sized membranous
30 substances of complicated shapes can be fabricated easily at low cost even when the lot size is small.

The reticulate material or bar-like material mentioned above may be fixed in position to cover the surface of a substrate in advance. The fixing method is not particularly restricted
35 but, depending on the intended application, may for example be

bolt-nut fixation or weld fixation. In this arrangement, a composite organic membranous substance rigidly secured to the substrate surface can be fabricated. The substrate surface is not particularly restricted but may for example be the surface of at least one member selected from among concrete, mortar and rock. The functions expected of the membranous substance are not particularly restricted but includes corrosion inhibition, water-proofing, reinforcement, prevention of slide-down, etc. of various structures such as concrete or mortar buildings, concrete ducts or conduits and other structures. The present invention is further applicable to the corrosion inhibition, water-proofing, water-leak prevention, reinforcement, prevention of collapsing or slide-down of various surfaces in civil engineering work, such as the surfaces of cliffs, tunnels, ponds, and waste disposal facilities, among others.

A typical applied technology is a method for corrosion-inhibition of concrete which comprises fixing said reticulate or bar-like material in position on a concrete surface in the first place, spray-coating the solvent-free two-component curable resin on said reticulate or bar-like material by the two-component collision-mixing spray coating technique, and allowing the resin to cure them and to thereby provide, over said concrete surface, a composite organic membranous substance comprising said reticulate or bar-like material partially embedded therein. In a repair project on the sewage system, for instance, the present invention can be applied to the anticorrosive treatment of the inner wall of the drainpipe or conduit. This can be carried out by fixing a cylindrical or hemicylindrical reticulate material on the inner wall of the drainpipe or an assembly of bars-like material affixed in parallel to a frame preformed in the shape complementary to the inner wall of the drainpipe and applying said resin. By this technique, the composite organic membranous substance of the invention can be securely attached to the concrete surface even when water exists on the concrete

surface, with the result that the work can be consummated in quite a brief period of time.

In the method of the invention, the composite organic membranous substance is fixed to a substrate such as concrete and the like material as an integral unit via the reticulate or bar-like material rigidly secured to the substrate surface. Therefore, even in the presence of water, the adverse results due to a reduction in the adhesion between the resin and the concrete surface can be prevented and a covering, corrosion-proofing, water-proofing or reinforcing work not entailing defects such as blisters, swelling, peeling, etc. can be consummated expediently and in a short period of time without being influenced by the surface water or moisture of concrete structures and other factors. Furthermore, since the method of the invention is a solvent-free technology, there is no risk for hazards to human health and environment.

The present invention, constituted as above, provides a technology by which even large-sized membranous substances of complicated shape can be fabricated easily at low cost. Moreover, by this technology, high-quality covering, corrosion-proofing, water-proofing, reinforcing and other field works can be carried out expediently and in short periods of time without being influenced by the surface water or moisture of concrete structures and other factors. Furthermore, the method of the present invention is comparatively safe to health and environment.

EXAMPLES

The following examples illustrate the present invention in further detail without defining the scope of the invention.

Example 1

As the solvent-free two-component curable resin, a

solvent-free 2-component polyurea resin system (Toughguard R-G, Nippon Paint) comprising an isocyanate component (A) and a polyamine component (B) was used. As the sprayer, a two-component collision-mixing sprayer (Gusmer) was used. The collision-mixing ratio of component (A)/component (B) was approximately 1:1 by volume and the NCO index, i.e. the ratio of amino groups in component (B) to isocyanate groups in component (A), was about 1.05. As the mixing spray gun, Gusmer's GX-7 gun was used. The material temperature was $55 \pm 5^\circ\text{C}$ for both components A and B and the delivery pressure condition was 7 to 12 MPa. As the reticulate material, a stainless steel mesh screen having a mesh size of 1 mm was used. The reticulate material was laid on a level ground and, with the spray gun being held at a distance of about 30 cm from the reticulate material and the resin-delivery direction being kept at right angles with the surface of the reticulate material, one side of the reticulate material was spray-coated.

The thickness of the resulting polyurea resin membrane was 2 to 3 mm on the coated side of the reticulate material. The applied resin had become dry tack-free by 5 seconds after coating.

The coated surface presented with a fine unevenness pattern corresponding to the meshes of the reticulate material but the coat was continuous and wholesome without evidence of pits, creases, discontinuities or cracks. Although the resin membrane was thus formed over the coated side of the reticulate material, there was little penetration of the resin on the reverse side of the reticulate material. The resin membrane could not be pulled off the reticulate material, with the two members forming an integral unit. Detailed observation revealed that the mesh material had been mainly covered with a resin membrane about the raised points of intersection thereof.

Examples 2 and 3

Except that the mesh size of the reticulate material was changed to 3 mm and 5 mm, respectively, the procedure of Example 1 was otherwise repeated to fabricate composite organic membranous substances. Each thickness of the polyurea
5 membranes thus formed was 2 to 3 mm and 3 to 4 mm, on the coated side of the reticulate material. The reverse side of the reticulate material was also formed with a resin membrane having a thickness of 2 to 3 mm in both cases.

In both cases, the coated side presented with a fine
10 unevenness pattern corresponding to the meshes but the resin membrane was continuous and wholesome without evidence of pits, creases, discontinuities or cracks. The resin covered not only the mesh material but also the reverse side thereof, with most part of the material being embedded in the resin to give a
15 composite organic membranous substance containing a mesh material as a core.

Example 4

Except that the mesh size of the mesh material was changed
20 to 10 mm, the procedure of Example 1 was otherwise repeated to fabricate a composite organic membranous substance. The thickness of the polyurea resin layer formed was 4 to 6 mm on the coated side of the material.

The coated side presented with a fine unevenness pattern
25 corresponding to the meshes but the membrane formed was continuous and wholesome without evidence of pits, creases, discontinuities or cracks. However, the resin enshrouded only the coated side of the reticulate material and did not cover the reverse side although the resin had emerged locally onto
30 the reverse side from the mesh. This is presumably because since the meshes were coarse, the fronts of the resin emerging out on the reverse side cured without conglomerating into a unit. The reticulate material and the resin membrane were integrated and could not be separated from each other. Detailed
35 observation revealed that the mesh screen had been mainly

covered with a resin membrane about the raised points of intersection thereof.

Example 5

5 Except that the mesh size of the material was changed to 3 mm and the tack-free time of the resin was adjusted to 20 seconds, the procedure of Example 1 was otherwise repeated to fabricate a composite organic membranous substance.

10 The coated side presented with a fine three-dimensional surface corresponding to the meshes but the resin membrane was continuous and wholesome without evidence of pits, creases, discontinuities or cracks. The resin covered up not only the coated side but also the reverse side so that most part of the reticulate material was integrally embedded in the resin
15 membrane.

Example 6

 Except that the polyamine for component (B) was partially replaced with a polyol to adjust the tack-free time of the system
20 to 120 seconds, a solvent-free two-component curable polyurethane/polyurea resin was prepared using the same isocyanate component (A) in otherwise the same manner as in Example 1. Then, using a reticulate material having a mesh size of 3 mm, a composite organic membranous substance was fabricated
25 in the same manner as in Example 1.

 The coated side presented with a fine unevenness pattern corresponding to the meshes but the membrane formed was continuous and wholesome without evidence of pits, creases, discontinuities or cracks. However, the resin covered only the
30 coated side of the reticulate material and did not cover the reverse side although the resin had emerged locally onto the reverse side. This is probably because the applied resin failed to be deposited in a sufficient amount to cover the reverse surface. The reticulate material and the resin membrane were
35 integrally joined and could not be separated from each other.

Detailed observation revealed that the mesh screen had been mainly covered with a resin membrane about the raised points of intersection thereof.

5 Example 7

 Except that the polyamine for component (B) was partially replaced with a polyol to adjust the tack-free time of the system to 180 seconds, a solvent-free two-component curable polyurethane resin was prepared using the same isocyanate
10 component (A) in otherwise the same manner as in Example 1. Then, using a material having a mesh size of 3 mm, a composite organic membranous substance was fabricated in the same manner as in Example 1.

 The coated side presented with a fine unevenness pattern
15 corresponding to the meshes but the membrane formed was continuous and wholesome without evidence of pits, creases, discontinuities or cracks. However, the resin covered only the coated side of the reticulate material and did not cover the reverse side although the resin had emerged locally onto the
20 reverse side. This is probably because since the tack-free time of this composition was rather long, the applied resin failed to be deposited in a sufficient amount to cover the reverse surface. The reticulate material and the resin membrane were integrally joined and could not be separated from each other.
25 Detailed observation revealed that the mesh screen had been covered with a resin membrane about the raised points of intersection thereof.

 Comparative Example 1

30 Except that the mesh size of the material was set to 15 mm, a composite organic membranous substance was fabricated in otherwise the same manner as in Example 1.

 The coated side failed to present with a continuous resin membrane, and the resin was not applied in a sheet form to the
35 reticulate material, so that the desired composite organic

membranous substance could not be provided. It was considered that because of the excessively large mesh size for the resin to be applied, the resin was not applied in a sheet form to the reticulate material.

5

Comparative Example 2

In the solvent-free two-component polyurethane resin used in Example 7, the amount of the tin catalyst was reduced to give a tack-free time of 30 minutes. This composition was
10 coated on a material having a mesh size of 3 mm in the same manner as in Example 1.

The coated side failed to present with a continuous resin membrane, and the resin was not applied in a sheet form to the reticulate material, so that the desired composite organic
15 membranous substance could not be provided. That is probably because the tack-free time of the resin was too long for the mesh size so that the resin was not applied in a sheet form to the reticulate material.

20 Comparative Example 3

An epoxy resin (Toughguard E top coat, Nippon Paint) was coated on a reticulate material having a mesh size of 3 mm. The tack-free time of the resin was 18 hours.

The coated side failed to present with a continuous
25 membrane, and the resin was not applied in a sheet form to the reticulate material, so that the objective composite organic membranous substance could not be obtained.

CLAIMS

1. A method of fabricating a composite organic
membranous substance comprising a membranous organic resin and
5 a reticulate or bar-like material,

which comprises coating a solvent-free two-component
curable resin on a reticulate or bar-like material in a sheet
form by two-component collision-mixing spray coating, and
allowing the resin to cure
10 and to thereby form a membranous organic resin integral with
said reticulate or bar-like material.

2. The method according to Claim 1
wherein the solvent-free two-component curable resin
15 comprises an isocyanate component (A) and a polyamine and/or
polyol component (B).

3. The method according to Claim 1 or 2
wherein the reticulate material has a mesh size of not
20 more than 10 mm.

4. The method according to any of Claims 1 to 3
wherein the solvent-free two-component curable resin has
a tack-free time of not more than 3 minutes.

25 5. The method according to any of Claims 1 to 4
wherein the membranous organic resin covers at least part
of the reticulate or bar-like material.

30 6. The method according to any of Claims 1 to 5
which comprises fixing said reticulate or bar-like
material in position over a substrate surface to be protected
and, then, forming said composite organic membranous resin to
cover said substrate surface.

35

7. The method according to Claim 6
wherein the substrate surface is at least one member
selected from among concrete, mortar and rock.

5 8. The method according to Claim 7
 wherein the solvent-free two-component curable resin
has a tack-free time of not more than 20 seconds.

 9. The method according to any of Claims 1 to 8
10 wherein the two-component collision-mixing type spray
coating is carried out at a collision-mixing pressure of 6 to
15 MPa by means of a high-pressure two-component collision-
mixing type sprayer with a mixing spray gun with a mechanical
self-cleaning function.

15 10. A method for corrosion-inhibition of concrete
 which comprises fixing a reticulate or bar-like material
in position on a concrete surface and coating a solvent-free
two-component curable resin over said reticulate or bar-like
20 material by two-component collision-mixing spray coating, and
allowing the resin to cure and
to thereby form, over said concrete surface, a composite thick
membranous organic resin comprising at least part of said
material.

25 11. A composite organic membranous substance fabricated
by the method according to Claim 1.